Real-time, *in situ* monitoring of surface reactions during plasma passivation of GaAs

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Real-time, *in situ* observations of surface chemistry during the remote plasma passivation of GaAs is reported herein. Using attenuated total reflection Fourier transform infrared spectroscopy, the relative concentrations of -As-O, -As-H, -H_2O, and -CH_2 bonds are measured as a function of exposure to the effluent from a microwave discharge through NH_3, ND_3, H_2, and D_2. The photoluminescence intensity (PL) from the GaAs substrate is monitored simultaneously and used qualitatively to estimate the extent of surface state reduction. It was found that, while the -CH_x($x = 2,3$) and -As-O concentrations are reduced rapidly, the rates at which the -As-H concentration and the PL intensity increase are relatively slow. The concentration of -H_2O on the GaAs surface increases throughout the process as surface arsenic oxides and the silica reactor walls are reduced by atomic hydrogen. These observations suggest that removal of elemental As by reaction with H at the GaAs–oxide interface limits the passivation rate.

The poor electronic properties of native-oxide-contaminated GaAs are well-known. Recently, surface cleaning and passivation processes have received well-deserved attention in an effort to improve the interface/surface integrity in GaAs-based devices.[1] The poor interface problem arises because As_2O_3 is thermodynamically unstable[2] in the presence of GaAs and reacts to form As according to

$$As_2O_3 + 2GaAs \rightarrow 4As + Ga_2O_3. \quad (1)$$

Elemental As produces in turn a near-midgap state that can pin the Fermi level and enhance nonradiative recombination. While wet chemical cleaning and passivation methods have shown considerable promise in reducing the surface state density,[3] these methods are not easily integrated into clustered processing schemes and present a larger environmental waste problem when compared to their "dry" plasma counterparts.[4–11] For these reasons, it is desirable to develop dry passivation and cleaning treatments for contaminated GaAs.

Using discharges through H-containing gases, such as H_2 or NH_3, arsenic oxides can be reduced according to[8]

$$12H + As_2O_3 \rightarrow 3H_2O + 2AsH_3. \quad (2)$$

However, optimization of such dry processes is challenging because of the large number of variables that can affect the outcome of the process. In plasma passivation of GaAs, one must first choose a reactor design and optimal processing conditions by resorting, usually, to laborious trial and error treatment and post-process analysis. Alternatively, the optimal exposure time and processing parameters can be determined rapidly using real-time, *in situ* monitoring.[10,11]

Because photoluminescence (PL) intensity is correlated with surface state density and Schottky barrier height,[12] it makes a useful qualitative metric with which plasma passivation processes can be rapidly optimized.[10,11] Using this approach, we developed plasma processes for stable passivation of GaAs at room temperature without introducing ion-induced damage. However, PL monitoring does not offer insight into the chemical changes that occur on the wafer surface during the plasma process. Such information is essential for understanding the mechanism responsible for passivation, for further process optimization, and for generalization to other systems and materials.

To gain this chemical insight, we turn to the technique of attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy[13] to monitor in real-time and *in situ* changes in -As-O, -As-H, -H_2O, and -CH_2 surface bonding resulting from exposure of native-oxide-contaminated GaAs to the effluent from microwave discharges through NH_3. Simultaneously, we monitor PL and correlate changes in PL with changes in surface bonding. We have also examined passivation processes using ND_3, H_2, and D_2 plasmas but report those results elsewhere.[14]

The reactor used in this work has been described previously.[10,11,15] Briefly, we pass NH_3 through a 25.4 mm diam quartz tube enclosed by an Evenson-type microwave cavity. After a 90° bend designed to minimize irradiation of the wafer by the plasma glow, the effluent from the plasma travels approximately 28 cm to the grounded wafer surface.[11] The sample temperature is held at 25 °C while the pressure is controlled using a throttling valve. Using an in-series ammeter, no net current could be measured at the wafer stage ($\lesssim 0.3$ nA), indicating that negligible ion and electron bombardment of the wafer takes place during the process. The base pressure of the system is $\sim 2 \times 10^{-7}$ Torr.

The double-sided polished semi-insulating GaAs samples are cleaved into 1×5 cm rectangular pieces whose ends are polished further to produce a 45° bevel (Fig. 1).

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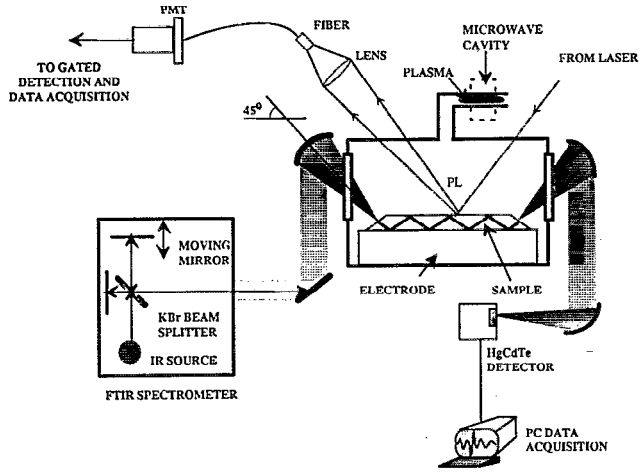

FIG. 1. Schematic illustration of apparatus used for simultaneous measurement of ATR-FTIR spectrum and PL intensity from beveled GaAs wafer during remote NH_3 plasma passivation.

The output from a Nicolet Model 510P FTIR spectrometer is passed through a N_2 purged beam path and focused at normal incidence onto one of the beveled faces of the GaAs crystal. The infrared beam undergoes 38 multiple internal reflections from the surface exposed to the plasma effluent as it passes through the crystal (Fig. 1). The infrared light is then collected using reflective optics and focused onto a liquid-nitrogen cooled HgCdTe detector whose output is Fourier transformed.

A pulsed, N_2-pumped dye laser at 500 nm is used to excite PL (Fig. 1),[10] which is collected and passed through a color filter into a fiber optic bundle. The output of the bundle is then coupled directly to a photomultiplier tube whose output is sampled synchronously with the exciting laser pulse using a gated integrator and displayed in real-time.

The ATR-FTIR spectrum shown in Fig. 2 is a ratio of infrared transmission after passivation to that before passivation of the GaAs. An increase in transmission results when the concentration of the absorbing surface bond is reduced as a result of plasma treatment. Conversely, transmission decreases when the surface concentration of a species increases. The spectral assignments indicated in Fig. 2 warrant some discussion. The As-O diatomic molecule has a characteristic vibrational frequency of 963 cm^{-1}.[16] Depending on how As is bound to other species on the surface, this stretching frequency will shift. For example, the IR absorption spectra of metal arsenites show bands from 750–900 cm^{-1}, and As_2O_3 minerals, arsenalite, and claudetite as well as As_2O_5 absorb infrared around 810–900 cm^{-1}.[17] Based on these shifts, we assign the band observed at $\sim$850 cm^{-1} to the -As-O stretch. Since the symmetric and antisymmetric C-H stretches of surface hydrocarbons, such as —CH_3 and =CH_2, occur between 2850 and 2960 cm^{-1},[18] and both sp^3 and sp^2 carbon are prevalent contaminants, we assign the bands centered at 2850 and 2912 cm^{-1} to be a superposition of $CH_x(x=2,3)$ stretches. With these assignments, we see that the concentrations of both -As-O and -CH_x species are reduced by exposure of contaminated GaAs to the hydrogen-containing plasma effluent. Ion bombardment is not needed to remove these species.

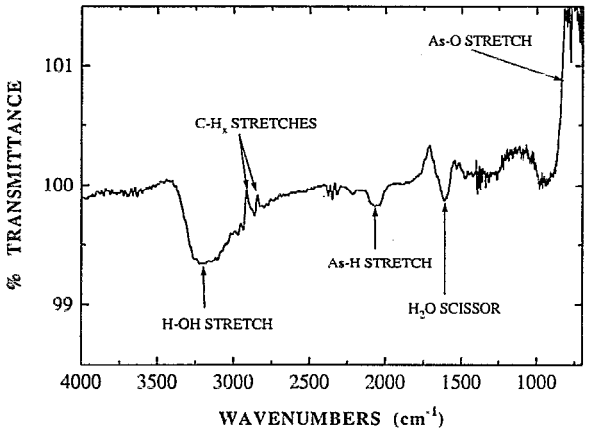

FIG. 2. Ratio of ATR-FTIR transmission after GaAs plasma passivation to that prior to passivation. Microwave power used was 140 W and the gas flow rate was 10 sccm.

The disappearance of -As-O is consistent with post-process, *ex situ* x-ray photoelectron spectroscopy (XPS) analysis[10,11] as well as the predictions of Capasso and Williams.[8] Because of overlapping with bulk phonon absorption at 773 cm^{-1}, we cannot detect changes in -Ga-O bonding, but we know from prior work using XPS that the concentration of -Ga-O actually increases as a result of exposure to the plasma effluent.[7,10,11]

In Fig. 2, the band at 2100 cm^{-1} is assigned to -As-H based on the work of Joseph *et al.*[19] who found that the spectrum exhibits bands for arsenic hydride from 1950 to 2150 cm^{-1}. The broadband at 3200 cm^{-1} is obtained in both NH_3 and H_2 plasma treatments and assigned to the -O-H stretch of -H_2O based on the low temperature work by Chabal and Christman.[20,21] Accompanying the broad absorption at 3200 cm^{-1} is the -H_2O scissor motion at 1600 cm^{-1}. Both these peaks shift to 2400 and 1180 cm^{-1}, respectively, when ND_3 or D_2 are substituted for NH_3 and H_2.[14] The concentrations of -As-H and -H_2O clearly increase as a result of the passivation process. The formation of water on the surface is expected from the reduction of arsenic oxides[8] while -As-H is a likely intermediate in the reduction of elemental As and arsenic oxides to form volatile AsH_3. Water also forms on the surface via reaction of H with the SiO_2 walls of the reactor.[14] In any case, water does not readily desorb from the passivated GaAs surface at room temperature; but, by pumping for many hours, it can be reduced and we conclude that some -H_2O may only be physisorbed.[14]

The rate at which -As-O disappears after the microwave discharge is turned on appears to be limited by the transport of H atoms to the surface. A simple estimate for the gas residence time yields $\sim$2 min, which is comparable to the characteristic time for removal of -As-O [Fig. 3(a)]. On the other hand, the formation of -As-H is significantly delayed from plasma initiation and is clearly not limited by the rate of H atom transport to the surface alone [Fig.

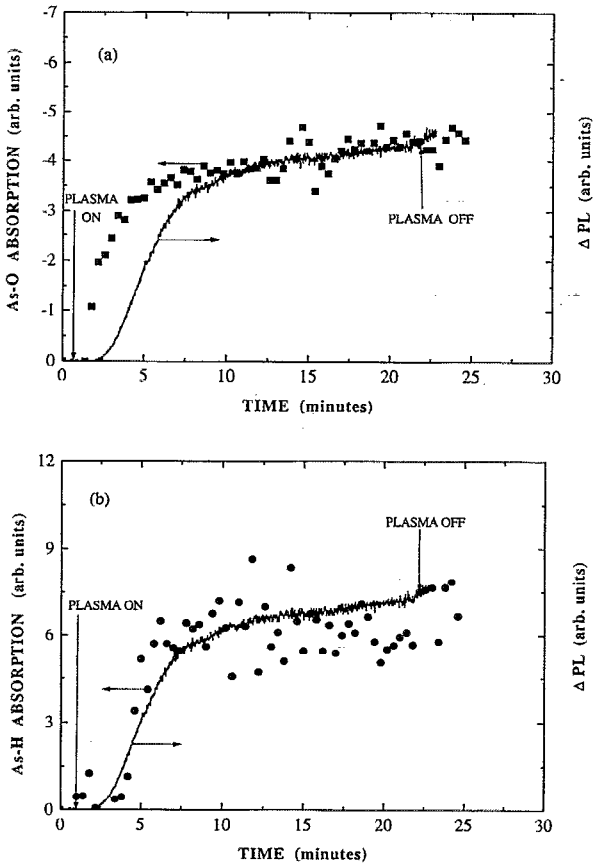

FIG. 3. Real-time changes in (a) -As-O and (b) -As-H absorption during remote NH_3 passivation of GaAs. Superimposed on both traces is the corresponding change in PL intensity. Note the delay in the onset of the PL and the -As-H absorption.

3(b)]. Interestingly, the enhancement in PL intensity is also delayed and follows the same functional dependence as the appearance of the -As-H bonds. Because As is formed at the interface between oxide and GaAs, it seems reasonable that the rates for -As-H formation and PL enhancement may be limited, at least in part, by the solid-state diffusion of H through the oxide layer. The buildup of water on the surface may further slow the diffusion of H to the interfacial As.

In summary, we report real-time, *in situ* monitoring of the chemical changes that take place on native-oxide-contaminated GaAs during passivation using the effluent from a NH_3 microwave discharge. By simultaneously monitoring PL intensity and ATR-FTIR absorption, we find that the onset of passivation is delayed along with the formation of -As-H bonds. By contrast, arsenic oxide is removed as fast as H atoms can be transported to the surface. A combination of H transport to the surface and H diffusion through the native-oxide layer is suggested as the rate limiting step for the surface passivation of GaAs.

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[21] We note that some of this absorption can arise from NH_3 physisorbed onto the surface with the -H_2O. This will be addressed in more detail in a future publication (Ref. 14).